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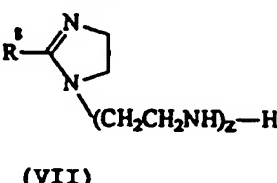
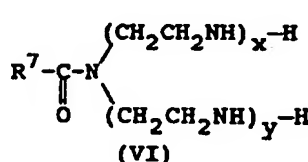
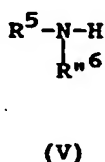
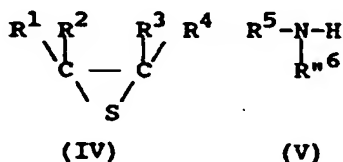
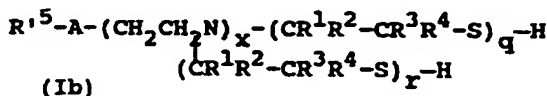
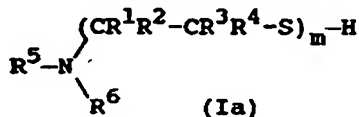
(54) Abstract Title

Use of mono- or polythiols as corrosion inhibitors

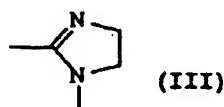
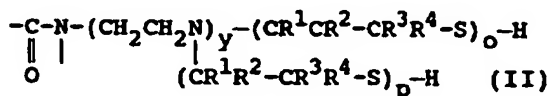
(57) The present invention relates to the use of a compound (Ia) or (Ib) or of the adduct of at least one

compound (IV) to at least one compound having at least one group -NH<sub>2</sub> or 

selected among aliphatic amines (V), amidoamines (VI) imidazolines (VII), as inhibitor of the corrosion of metals, particularly of the carbonic and/or sulfhydryl corrosion of the carbon steels in the oil industries.



R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> = H, alkyl group having 1 to 10 carbon atoms or aromatic group; R<sup>5</sup> = alkyl or alkenyl group having 8 to 30 carbon atoms; R<sup>6</sup> = alkyl group having 1 to 30 carbon atoms or alkenyl group having 2 to 30 carbon atoms, or a -(CR<sup>1</sup>R<sup>2</sup>-CR<sup>3</sup>R<sup>4</sup>-S)<sub>n</sub>-H group; m, n = integer from 1 to 10; R<sup>15</sup> = alkyl or alkenyl group having 7 to 29 carbon atoms; A = group (II) bound to R<sup>15</sup> by -CO-, or group (III) bound to R<sup>15</sup> by the carbon atom:



x, y = 0 or integer from 1 to 10 where 1 ≤ x + y ≤ 10; q, r, o, p = average number of -CR<sup>1</sup>R<sup>2</sup>-CR<sup>3</sup>R<sup>4</sup>-S- chains; R<sup>16</sup> = H or alkyl or alkenyl group; R<sup>7</sup> and R<sup>8</sup> are the same as R<sup>5</sup>; z = 0 or integer from 1 to 10.

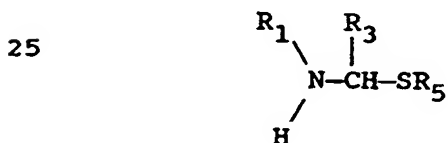
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USE OF AMINO GROUP-CONTAINING THIOLS AS INHIBITORS OF THE  
CORROSION OF METALS.

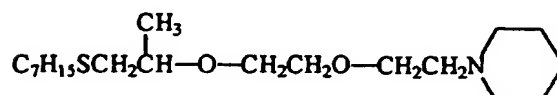
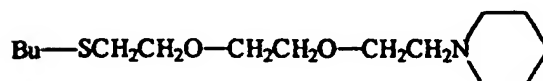
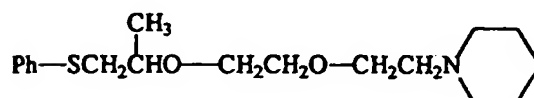
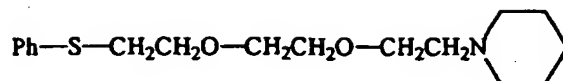
The present invention relates to the protection of  
metals against corrosion, particularly against corrosion of  
5 equipments for oil production, transport, storage and  
refining, said equipments being generally made of carbon  
steel.

At the present time, such a protection is mainly  
provided by the use of corrosion inhibitors based on organo-  
10 nitrogenated compounds, such as amines, quaternary ammonium  
derivatives, amidoamines and imidazolines, or based on  
phosphoric esters.

Furthermore it is known that the addition of  
elementary sulphur may improve the corrosion  
15 inhibitory efficiency of organo-nitrogenated compounds  
(DE-A-3 437 936). Also, mixtures of organo-sulphurated  
compounds and organo-nitrogenated compounds were cited  
as efficient corrosion inhibitors (US-A-5 368 774 ;  
US-A-4 295 979 ; US-A-4 446 056). Also, compounds  
20 containing both sulphur and nitrogen in their molecule were  
proposed as corrosion inhibitors : thus, US-A-4 633 019  
describes, as corrosion inhibitors, the compounds of  
formula :



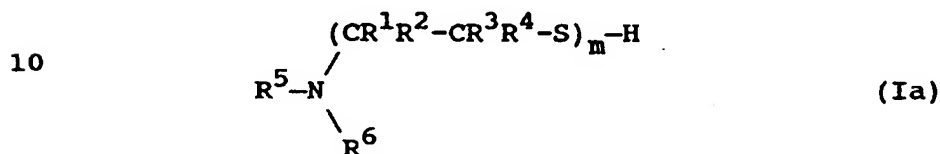
wherein  $R_1$  stands for an alkyl, cycloalkyl ou hydroxyalkyl  
30 group having 1 to 18 carbon atoms ;  $R_3$  stands for an alkyl  
group having 1 to 4 carbon atoms ; and  $R_5$  stands for an  
alkyl group having 1 to 18 carbon atoms ; and Movsum-Zadz,  
M.M. ; Mamedov F.N. ; Sultanova, N.R. ; Dzhaferova N.V., in  
Korroz. Zashch. Neftegazov. Prom-sti. (1980), (10), 8-10,  
35 describe the following compounds :



as corrosion inhibitors

It has now been discovered a novel family of compounds that have a corrosion inhibitory efficiency particularly in the oil industry, which is even higher than  
5 the compounds known until now.

A first object of the present invention is the use of a mono- or polythiol selected among those of formula (Ia) :

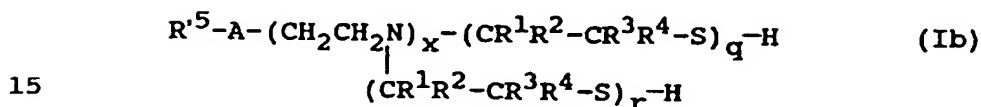


wherein :

- 15 - each of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  independently stands for a hydrogen atom, an alkyl group having 1 to 10 carbon atoms or an aromatic group, it being possible for substituents  $\text{R}^1$  and  $\text{R}^3$  (or  $\text{R}^2$  and  $\text{R}^4$ ) to be mutually bound to form a hydrocarbon ring together with both  
20 carbon atoms which bear them ;

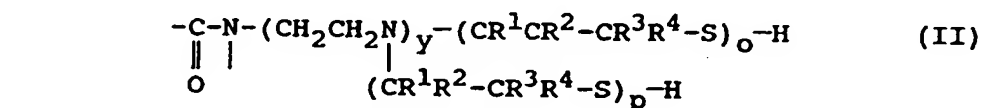
- $R^5$  stands for a straight or branched alkyl or alkenyl group having 8 to 30 carbon atoms ; and
- $R^6$  stands for a straight or branched alkyl group having 1 to 30 carbon atoms, or a straight or branched alkenyl group having 2 to 30 carbon atoms, or a  $-(CR^1R^2-CR^3R^4-S)_n-H$  group ;
- $m$  and  $n$ , which are identical or different, each represent an integer in the range of 1 to 10, wherein the total number  $m + n$  of  $-CR^1R^2-CR^3R^4-S-$  chains, identical or different, can be as high as 20, preferably as high as 10 ;

and those of formula (Ib) :

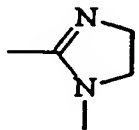


wherein :

- $R^1, R^2, R^3$  and  $R^4$  are as defined above ;
- $R^5$  stands for a straight or branched alkyl or alkenyl group having 7 to 29 carbon atoms, for example 7 to 19 carbon atoms ; and
- $A$  stands for a group (II) :



- bound to  $R^5$  by  $-CO-$  ;  
or a group (III) :

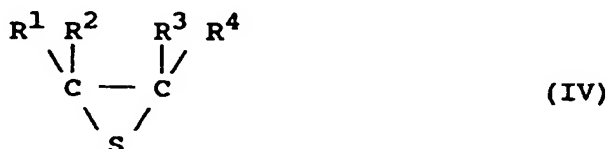


(III)

- bound to  $R^5$  by the carbon atom ;
- $x$  and  $y$ , identical or different, represent each 0 or an integer in the range of 1 to 10, with the proviso that  $1 \leq x + y \leq 10$  ;

- each of q, r, o and p is an average number of  $-CR^1R^2-CR^3R^4-S-$  chains, it being possible for said average number to be 0 and for said chains to be the same or different, for the "r" to be different if x is higher than 1 and for the "p" to be different if y is higher than 1, and "q +  $\sum r + o + \sum p$ " in the case where A is a group (II) or "q +  $\sum r$ " in the case where A is a group (III) is higher than 0 and can be as high as 30, especially in the range of 0.5 to 10 ;

10 or of the adduct of at least one compound of formula (IV) :



15

wherein each of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are as defined above, to at least one compound having at least one group  $-NH_2$  or

20  $\backslash$   
NH, selected among :  
/

(a) aliphatic amines of formula (V) :



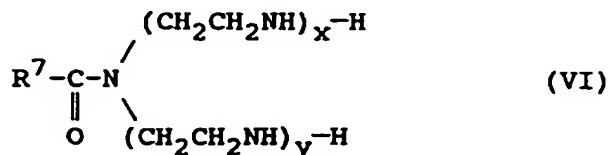
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wherein :

- $R^5$  is as defined above ; and
- $R^{*6}$  stands for a hydrogen atom or a straight or branched alkyl group having 1 to 30 carbon atoms or a straight or branched alkenyl group having 2 to 30 carbon atoms ;

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(b) amidoamines of formula (VI) :



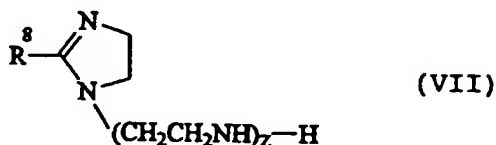
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wherein :

- $R^7$  has the same meaning as  $R^{15}$  ;
- x and y are as defined above ; and

(c) imidazolines of formula (VII) :

5



wherein :

- $R^8$  has the same meaning as  $R^{15}$  ; and
- z stands for 0 or is an integer in the range of 1 to 10 ;

10

as inhibitor of the corrosion of metals, particularly as inhibitor of the carbonic and/or sulfhydryl corrosion of the carbon steels in the oil industries.

The inhibitor of the corrosion of metals according to the present invention can be preferably used under acidic conditions of not more than pH 6.

Particularly, each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  independently stands for a hydrogen atom, an alkyl group having 1 to 8 carbon atoms or a phenyl group, it being possible for  $R^1$  and  $R^3$  (or  $R^2$  and  $R^4$ ) to be mutually bound to form an alkylene chain.

In the formula (Ia),  $R^5$  can especially stand for the residue of a primary complex fatty amine, such as a copra chain or an oleic chain,  $R^6$  standing then for a  $-(CR^1R^2-CR^3R^4-S)_n-H$  group, the resulting dithiol being then under the form of a mixture ;  $R^5$  and  $R^6$  can also simultaneously stand for residues of a secondary complex fatty amine (being each for example a copra chain), the resulting monothiol being then under the form of a mixture.

In the formula (Ib),  $R^{15}$  can also stand for the residue of an amide of a complex fatty acid, the resulting mono- or polythiol being then under the form of a mixture.

The adduct may also consist in the adduct of compound(s) (IV) to a mixture of compound (VI) and of compound (VII) consisting of a product of the dehydration

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condensation reaction of a fatty acid with a polyamine under production of an amidoamine and partial ring closure of the latter into imidazoline.

The compound of formula (IV) is selected particularly among ethylene sulfide, propylene sulfide, 1,2-dimethyl thirane, 2,2-dimethyl thirane, n-octyl thirane, cyclohexene sulfide, styrene sulfide and 1,2-diphenyl thirane.

The amines of formule (V) are selected for example among decyl amine, undecyl amine, lauryl amine, myristyl amine, cetyl amine, stearyl amine, primary amines derived from a fatty acid obtained from a coconut oil, primary amines derived from oleic acid, primary amines derived from a fatty acid obtained from a soybean oil, didecyl amine, diundecyl amine, dilauryl amine, dimyristyl amine, dicetyl amine, distearyl amine, secondary amines derived from a fatty acid obtained from a coconut oil, secondary amines derived from oleic acid and secondary amines derived from a fatty acid obtained from a soybean oil.

The amidoamines of formula (VI) are selected particularly among :

- monoamide of lauric acid with ethylene diamine ;
  - amide of lauric acid with diethylene triamine ;
  - amide of lauric acid with triethylene tetramine ;
  - amide of lauric acid with tetraethylene pentamine ;
- and the analogous of amides with stearic acid, oleic acid, fatty acid derived from coconut oil and fatty acid derived from soybean oil.

The imidazolines of formula (VII) are selected particularly among :

- . 2-undecyl imidazoline ;
- . 1-(2-aminoethyl)-2-undecyl imidazoline ;
- . 1-[N-(2-aminoethyl)-2-aminoethyl]-2-undecyl imidazoline ;
- . 2-heptadecyl imidazoline ;
- . 1-(2-aminoethyl)-2-heptadecyl imidazoline ;

- 1-[N-(2-aminoethyl)-2-aminoethyl]-2-heptadecyl imidazoline ;
- imidazolines produced dehydration and ringclosure of :
  - 5 • amide of lauric acid with tetraethylene pentamine ;
  - amide of stearic acid with tetraethylene pentamine ;
  - monoamide of oleic acid with ethylene diamine ;
  - 10 • amide of oleic acid with diethylene triamine ;
  - amide of oleic acid with triethylene tetramine ;
  - amide of oleic acid with tetraethylene pentamine ;
  - amide of fatty acid derived from coconut oil with triethylene tetramine ;
  - 15 • amide of fatty acid derived from coconut oil with tetraethylene pentamine ;
  - monoamide of fatty acid derived from soybean oil with ethylene diamine ;
  - 20 • amide of fatty acid derived from soybean oil with diethylene triamine ;
  - amide of fatty acid derived from soybean oil with triethylene tetramine ;
  - amide of fatty acid with tetraethylene pentamine.

25 In the adducts of the invention, the compound of formula (IV) has been added in particular at the rate of 1 to 20 moles for 1 mole of (a) ; and from 0.5 to 30 moles for 1 mole of (b) or (c).

30 The addition reaction leading to the products of the invention is generally carried out in an organic solvent which is inert under the conditions of the reaction ; however, the use of a solvent may be omitted. As concrete examples of the organic solvents which are usable herein, aromatic compounds such as benzene, toluene and xylene ;  
 35 ether type compounds such as diethyl ether, ethyl isobutyl ether, tetrahydrofuran and dioxane ; alcohol type compounds such as methanol, ethanol, n-propanol, isopropanol, n-

butanol, t-butanol, heptanol, 2-ethyl hexanol and cyclohexanol ; nitrile type compounds such as acetonitrile and benzonitrile, amide type compounds such as N,N-dimethylformamide and N-methylpyrrolidone, and dimethyl sulfoxide may be cited.

The reaction temperature, although it is not particularly defined, is generally in the range of 10 to 200°C, preferably, in the range of 50 to 120°C.

Adducts which are especially preferred for the application of the invention are:

- the adduct of 2 moles of ethylene sulfide to one mole of lauryl amine ; and
- the adduct of about 2 to 3 moles of ethylene sulfide to 2-aminoethyl dodecanamide.

Another object of the present invention is a composition for the protection of metals against corrosion, particularly for the protection of carbon steels against carbonic and/or sulfhydrylic corrosion in oil industries, characterized by the fact that it consists in or comprises a solution in at least one organic solvent of at least one mono- or polythiol and/or at least one adduct as defined above, when it is intended to be used in a corrosive medium consisting of an oily phase, said composition further comprising at least one surfactant when it is intended to be used in a corrosive medium consisting of an aqueous phase or consisting of an aqueous phase and an oily phase.

Such a composition, intended to be used in a corrosive medium consisting of an oily phase, may consist of or comprise, for 100 parts by weight :

- (A) 20 to 50 parts by weight of at least one mono- or polythiol and/or at least one adduct as defined above ; and
- (B) 50 to 80 parts by weight of at least one organic solvent selected particularly among the alcohols such as those previously cited, the glycol mono- or diethers such as the di- or tri-ethylene glycol and the propylene glycol, petroleum fractions such as the white spirit, the fuel oils, the kerosene and the naphtha.

Such a composition, intended to be used in a corrosive medium consisting of an aqueous phase or consisting of an aqueous phase and an oily phase, may consist of or comprise, for 100 parts by weight of (A) + (B)

5 + (C) :

(A) 20 to 40 parts by weight of at least one mono- or polythiol and/or at least one adduct as defined above ;

(B) 40 to 20 parts by weight of at least one organic solvent selected particularly among the glycol ethers, in particular the butyl glycol ; and

(C) 20 to 40 parts by weight of at least one surfactant, selected particularly among aminoacides having a fatty chain and oxyethylenated (2 to 20 units) derivatives of fatty amines (tallow or copra).

15 The present invention also relates to a method for the protection of metals against corrosion, particularly of carbon steels against carbonic and/or sulfhydrylic corrosion in oil industries, characterized by the fact said metals are treated by a composition as defined above, at a temperature  
20 comprised between room temperature and 180°C, preferably of about 120°C.

The following Examples illustrate the present invention without however restrict the scope thereof. They are preceded by Reference Examples A to T which describe the  
25 preparation of the compounds or products of the invention A to T respectively, and in which the following abbreviations have been used :

ES : ethylene sulfide

DMF : N,N-dimethylformamide

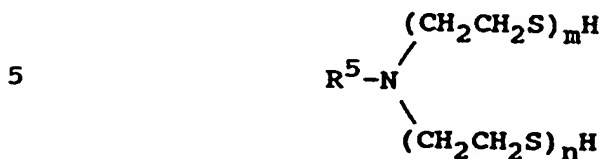
30 AEDAM : 2-aminoethyl dodecanamide

AEOAM : 2-aminoethyl octadecanamide.

The average number of moles of ES added to one mole of amine (a) (Examples A-H and S-T) or of amidoamine (b) (Examples I-L) or of mixture of amidoamine (b) and  
35 imidazoline (c) (Examples M to R) was calculated on the basis of the <sup>1</sup>H RMN analysis.

\*  
\* \*

Reference Examples A to H describe the preparation of compounds of formula :



obtained by the addition of  $m + n$  moles of ES on one mole of primary amine (a) of formula  $\text{R}^5\text{NH}_2$ .

10 Reference Example A :  $\text{R}^5 = n\text{-C}_{12}\text{H}_{25}$  and average value of  $m + n = 2$

In a three-neck flask provided with a stirring device, a thermometer, a reflux condenser, and a dropping funnel, 30.0 g (162 mmols) of lauryl amine and 49.5 g of dioxane were placed, heated to 107°C and refluxed. To the resultant reaction mixture kept at this temperature, 19.5 g (324 mmols) of ES were added dropwise over a period of four hours. After the dropwise addition was completed, the combined compounds were left reacting at the same temperature for 4 hours. After the reaction was completed, the resultant reaction solution was distilled to expel the solvent by evaporation, to obtain 48.2 g of a colorless transparent liquid (yield = 97%).

25 Reference Example B :  $\text{R}^5 = \text{C}_{12}\text{H}_{25}$  and average value of  $m + n = 5$

In a three-neck flask provided with a stirring device, a thermometer, a reflux condenser, and a dropping funnel, 30.0 g (92 mmols) of the ES adduct of lauryl amine (average number of added ES of 2.3) obtained by substantially the same procedure as in Reference Example A, 25.0 g of acetonitrile, and 5.0 g of dioxane were placed and heated to 78°C. To the resultant reaction mixture kept at

this temperature, 16.6 g (276 mmols) of ES were added dropwise over a period of 40 minutes. After the dropwise addition was completed, the combined compounds were left reacting at the same temperature for 3.5 hours. After this  
 5 reaction was completed, the resultant reaction solution was returned to normal room temperature and filtered to expel 4.8 g of white solids insoluble in the solvent. The filtrate was distilled to expel the solvent, to obtain 40.5 g of a light yellow waxy product (yield = 87%).

10 Reference Example C :  $R^5 = n-C_{18}H_{37}$  and average value of  $m + n = 2.3$

A white waxy product was obtained in the amount of 44.0 g (yield = 78%) by the procedure of Reference Example A while using 30.8 g (111 mmols) of stearyl amine and 25.4 g  
 15 (423 mmols) of ES as the reactants and 44.7 g of dioxane as the solvent.

Reference Example D :  $R^5 = n-C_{18}H_{37}$  and average value of  $m + n = 4.85$

When operating as described in Reference Example  
 20 C with more ES, a product D with an average value  $m + n$  of 4.85 was obtained.

Reference Example E :  $R^5 =$  coprah chain and average value of  $m + n = 2$

A slightly whitely turbid liquid was obtained in  
 25 the amount of 38.9 g (yield = 73%) by the procedure of Reference Example A while using 25.0 g (124 mmols) of an aliphatic primary amine originating in a coconut oil (total amine content of 4.98 meq/g determined by non-aqueous titration) and 28.4 g (472 mmols) of ES as the reactants and  
 30 53.4 g of dioxane as the solvent.

Reference Example F :  $R^5$  = coprah chain and average value of  $m + n = 4.6$

This product was obtained when operating as in the preceding Example using more ES.

5 Reference Example G :  $R^5$  = oleic chain and average value of  $m + n = 1.9$

A reddish brown liquid was obtained in the amount of 36.3 g (yield = 94%) by the procedure of Reference Example A while using 25.0 g (92 mmols) of an aliphatic  
10 primary amine originating in oleic acid (total amine content of 3.69 meq/g, determined by a non-aqueous titration) and 13.8 g (230 mmols) of ES as the reactants and 38.8 g of dioxane as the solvent.

15 Reference Example H :  $R^5$  = oleic chain and average value of  $m + n = 4.8$

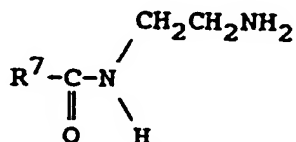
This product was obtained when operating as in the previous Example using more ES.

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\*  
\* \*

Reference Examples I to L describe the preparation of adducts of p moles of ES to an amidoamine (b) :

25



Reference Example I :  $R^7$  =  $n\text{-C}_{11}\text{H}_{23}$  ; average value of  $p = 2.7$

30

In a four-neck flask having an inner volume of 500 ml. and provided with a stirrer, a thermometer, and a Dimroth condenser, 60.0 g of AEDAM and 180 g of dioxane were

placed and heated to 101°C as kept in an ambience of nitrogen. To the solution kept at this temperature, 44.6 g of ES placed in a dropping funnel (AEDAM/ES = 1/3.0 by molar ratio) were added dropwise over a period of 7 hours. After  
 5 the dropwise addition was completed, the reaction which ensued was allowed to proceed at the same temperature for 1.5 hour. After the reaction was completed, the reaction solution was allowed to cool to room temperature and filtered to remove a small amount of insolubles (0.3 g).  
 10 The filtrate was subjected to vacuum distillation to expel the solvent by vaporization and obtain 98.8 g of a light yellow waxy product (yield = 95%).

Reference Example J :  $R^7 = n-C_{11}H_{23}$  ; average value of  $p = 5.6$

15 In a four-neck flask having an inner volume of 200 ml and provided with a stirrer, a thermometer, and a Dimroth condenser, 38.0 g of the product obtained in Reference Example I, 57 g of DMF, and 57 g of dioxane were placed and heated to 101°C as kept in an ambience of  
 20 nitrogen. To the solution kept at this temperature, 16.9 g of ES placed in a dropping funnel were added dropwise over a period of 2.5 hours. After the dropwise addition was completed, the reaction which ensued was allowed to proceed at the same temperature for 0.5 hour. After the reaction  
 25 was completed, the reaction solution was allowed to cool to room temperature and filtered to remove an extremely small amount of insolubles. The filtrate was subjected to vacuum distillation to expel the solvent by vaporization and obtain 54.6 g of a light yellow waxy product (yield = 99%).

30 Reference Example K :  $R^7 = n-C_{17}H_{35}$  and average value of  $p = 2.7$

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a thermometer, and a

Dimroth condenser, 80.0 g of AEOAM and 240 g of dioxane were placed and heated to 103°C as kept in an ambience of nitrogen. To the solution kept at this temperature, 36.8 g of ES (AEOAM/ES = 1/2.5 by molar ratio) placed in a dropping  
 5 funnel were added dropwise over a period of 4 hours. After the dropwise addition was completed, the reaction which ensued was allowed to proceed at the same temperature for 7 hours. After the reaction was completed, the reaction solution was subjected to vacuum distillation to expel the  
 10 solvent by vaporization and then concentrated to about one half of the original volume to induce precipitation of insolubles, which were removed (21.5 g in amount) by filtration. The filtrate was subjected to vacuum distillation to expel the solvent by vaporization and obtain  
 15 94.0 g of a light yellow waxy product (yield = 80%).

Reference Example L :  $R^7 = n-C_{17}H_{35}$  and average value of  $p = 5.5$

In a four-neck flask having an inner volume of  
 20 200 ml and provided with a stirrer, a thermometer, and a Dimroth condenser, 40.0 g of the product obtained in Reference Example K, 60 g of DMF, and 60 g of dioxane were placed and heated to 105°C as kept in an ambience of  
 25 nitrogen. To the solution kept at this temperature, 14.7 g of ES placed in a dropping funnel were added dropwise over a period of 2 hours. After the dropwise addition was completed, the reaction which ensued was allowed to proceed at the same temperature for 0.5 hour. After the reaction  
 30 was completed, the reaction solution was subjected to vacuum distillation to expel the solvent by vaporization and obtain 54.6 g of a light yellow waxy product (yield = 99%).

\*  
\* \* \*

Reference Examples M to R describe the preparation  
 35 of adducts of ES to a product (d) obtained by condensation and deshydration of a fatty acid with a polyamine, such as defined in the following Table 1.

Tableau 1

Reference Example	Product d	Fatty acid	Polyamine	Primary amine* (meq/g)	Secondary amine* (meq/g)	Tertiary amine* (meq/g)	Imidazoline** (8 by weight)
M	d1	Fatty acid of copra oil	Diethylene triamine	1.634	1.697	3.034	76
N	d2	Fatty acid of copra oil	Triethylene tetramine	3.812	3.085	2.462	68
O	d3	Fatty acid of copra oil	Tetraethylene pentamine	5.908	2.467	3.239	45
P	d4	Oleic acid	Diethylene triamine	1.871	2.193	1.945	64
Q	d5	Oleic acid	Triethylene tetramine	2.961	1.579	2.796	72
R	d6	Oleic acid	Tetraethylene pentamine	4.359	3.121	2.313	66

\* Amounts found by non-aqueous titration

\*\* Percentage found by <sup>1</sup>H NMR

Reference Example M

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a thermometer, and a Dimroth condenser, 68.3 g (339.1 meq of active amine per equivalent weight of hydrogen) of product (d1) and 273.3 g of dioxane were placed and heated to 102°C as kept in an  
5      ambience of nitrogen. To the solution kept at this temperature, 21.3 g of ES placed in a dropping funnel were added dropwise over a period of 5 hours. After the dropwise  
10     addition was completed, the reaction which ensued was allowed to proceed at the same temperature for 1.5 hour. After the reaction was completed, the reaction solution was allowed to cool to room temperature and filtered to remove insolubles (12.1 g). The filtrate was subjected to vacuum  
15     distillation to expel the solvent by vaporization and obtain 77.5 g of a light yellow waxy product (yield = 86%).

The  $^1\text{H}$  NMR analysis showed that the average number of moles of ES added per one mole of (d1) was 0.7 and that the imidazoline content of the obtained product was 74% by  
20     weight.

Reference Example N

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a thermometer, and a Dimroth condenser, 70.6 g (756.1 meq of active amine per  
25     equivalent weight of hydrogen) of product (d2) and 280 g of dioxane were placed and heated to 104°C as kept in an ambience of nitrogen. To the solution kept at this temperature, 45.4 g of ES placed in a dropping funnel were added dropwise over a period of 6 hours. After the dropwise  
30     addition was completed, the reaction which ensued was allowed to proceed at the same temperature for one hour. After the reaction was completed, the reaction solution was allowed to cool to room temperature and filtered to remove insolubles (32.3 g). The filtrate was subjected to vacuum

distillation to expel the solvent by vaporization and obtain 83.2 g of a yellow waxy product (yield = 72%).

The  $^1\text{H}$  NMR analysis showed that the average number of moles of ES added per one mole of (d2) was 1.8 and that the imidazoline content of the obtained product was 61% by weight.

#### Reference Example O

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a thermometer, and a Dimroth condenser, 65.0 g (929.0 meq of active amine per equivalent weight of hydrogen) of product (d3) and 267.5 g of dioxane were placed and heated to 102°C as kept in an ambience of nitrogen. To the solution kept at this temperature, 55.9 g of ES placed in a dropping funnel were added dropwise over a period of 6 hours. After the dropwise addition was completed, the reaction which ensued was allowed to proceed at the same temperature for 0.5 hour. After the reaction was completed, the reaction solution was allowed to cool to room temperature and filtered to remove insolubles (28.6 g). The filtrate was subjected to vacuum distillation to expel the solvent by vaporization and obtain 92.1 g of a yellow turbid liquid product (yield = 76%).

The  $^1\text{H}$  NMR analysis showed that the average number of moles of ES added per one mole of (d3) was 2.5 and that the imidazoline content of the obtained product was 26% by weight.

#### Reference Example P

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a thermometer, and a Dimroth condenser, 75.75 g (929.0 meq of active amine per equivalent weight of hydrogen) of product (d4) and 303.9 g of dioxane were placed and heated to 102°C as kept in an ambience of nitrogen. To the solution kept at this

temperature, 48.6 g of ES placed in a dropping funnel were added dropwise over a period of 5 hours. After the dropwise addition was completed, the reaction which ensued was allowed to proceed at the same temperature for 0.5 hour.

- 5 After the reaction was completed, the reaction solution was allowed to cool to room temperature and filtered to remove insolubles (36.4 g). The filtrate was subjected to vacuum distillation to expel the solvent by vaporization and obtain 87.7 g of a yellow turbid liquid product (yield = 71%).

- 10 The NMR analysis showed that the average number of moles of ES added per one mole of (d4) was 1.3 and that the imidazoline content of the product obtained was 64% by weight.

#### Reference Example Q

- 15 In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a thermometer, and a Dimroth condenser, 71.6 g (537.1 meq of active amine per equivalent weight of hydrogen) of product (d5) and 286.4 g of dioxane were placed and heated to 104°C as kept in an
- 20 ambience of nitrogen. To the solution kept at this temperature, 48.4 g of ES placed in a dropping funnel were added dropwise over a period of 7 hours. After the dropwise addition was completed, the reaction which ensued was allowed to proceed at the same temperature for 1 hour.
- 25 After the reaction was completed, the reaction solution was allowed to cool to room temperature and filtered to remove insolubles (39 g). The filtrate was subjected to vacuum distillation to expel the solvent by vaporization and obtain 79.8 g of a yellow turbid liquid product (yield = 67%).

- 30 The NMR analysis showed that the average number of moles of ES added per one mole of (d5) was 1.2 and that the imidazoline content of the product obtained was 68% by weight.

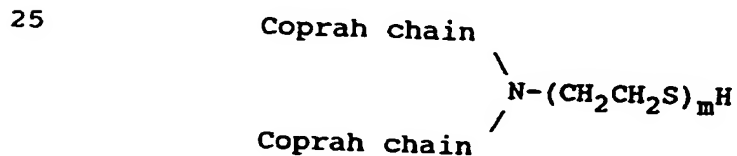
Reference Example R

In a four-neck flask having an inner volume of 500 ml and provided with a stirrer, a thermometer, and a Dimroth condenser, 73.1 g (862.5 meq of active amine per equivalent weight of hydrogen) of product (d6) and 291.4 g of dioxane were placed and heated to 103°C as kept in an  
 5 ambience of nitrogen. To the solution kept at this temperature, 52.0 g of ES placed in a dropping funnel were added dropwise over a period of 5 hours. After the dropwise  
 10 addition was completed, the reaction which ensued was allowed to proceed at the same temperature for two hours. After the reaction was completed, the reaction solution was allowed to cool to room temperature and filtered to remove insolubles (40.5 g). The filtrate was subjected to vacuum  
 15 distillation to expel the solvent by vaporization and obtain 84.1 g of a yellow turbid liquid product (yield = 67%).

The NMR analysis showed that the average number of moles of ES added per one mole of (d6) was 1.8 and that the imidazoline content of the product obtained was 74% by  
 20 weight.

\*  
\*   \*  
\*

Reference Examples S and T describe the preparation of compounds of formula :



30    obtained by the addition of m moles of ES to a secondary amine (a) of formula R<sup>5</sup>R<sup>6</sup>H with R<sup>5</sup> = R<sup>6</sup> = copra chain.

Reference Example S : average value of  $m = 1.7$

A whitely turbid liquid was obtained in the amount of 31.8 g (yield 84%) by the procedure of Reference Example A while using 30.0 g (65 mmols) of an ES adduct  
 5 (average number of moles of ES added = 0.75) of an aliphatic secondary amine originating in a coconut oil obtained substantially in the same manner as in Reference Example A and 7.8 g (130 mmols) of ES as the reactants and 18.9 g of dioxane and 18.9 g of DMF as the solvents.

10 Reference Example T : average value of  $m = 1$

This product was obtained when operating as in Example S using less ES.

#### EXAMPLE 1

The corrosion inhibitory efficiencies in carbonic  
 15 corrosion of compounds A to T were estimated by the measure of the instantaneous corrosion rate of a test piece made of carbon steel by the method of Tafel plots "Structural effect of quaternary ammonium group on inhibition on steel", D. Bernard, M. Haim and T.E. Pou. Proceeding of the 6th  
 20 European Symposium on Corrosion Inhibitors (6SEIC) Ann. Univ. Ferrara, N.S., Sez. V, Suppl. N.8, P. 1497, 1985)).

The tests were carried out in a 600 ml cell made of thermal glass (Pyrex) and having a gas inlet, a gas outlet and three electrodes fixed to the cell by ground  
 25 joints, namely :

- a working electrode made of carbon steel, the surface of which in contact with the corrosive solution being of  $1 \text{ cm}^2$  ;
- a saturated calomel reference electrode ; and
- 30 - a platinum counter-electrode having a very wide surface of contact with the solution.

In the cell, 500 ml of the corrosive solution are introduced. The corrosive medium is constituted by a 50 g/l solution of NaCl plus 0.25 g/l of acetic acid. Then, the counter-electrode and the reference electrode are introduced. The solution is deaerated by nitrogen bubbling during 1 hour and the solution is saturated by bubbling during 1 supplemental hour either CO<sub>2</sub> or H<sub>2</sub>S, according to the type of corrosion to be investigated. The tests were carried out at room temperature.

The compounds A to T were used in a solubilized state or as dispersed in isopropyl alcohol before being added in the corrosive medium.

When conducting each test, a solution or a dispersion of the compound to be tested is introduced in order to have a concentration of this latter in the corrosive medium. Then, the measuring electrode is dipped in said corrosive medium. The corrosion potential is examined. When the latter is steady, the experience is started according to the following parameters :

- 20 start potential = -1000 millivolts with respect to the potential of the reference electrode
- final potential = 100 millivolts with respect to the corrosion potential
- potential
- 25 sweep rate = 1 millivolt per second.

The corrosion current ( $i_{\text{corr}}$ ) is determined by intersection of the anodic and cathodic Tafel plots (see above cited literature reference).

The protection percentage (% P), which shows the corrosion inhibitory efficiency of a compound, is given by :

$$\% P = (i_{\text{corr}}^0 - i_{\text{corr}} / i_{\text{corr}}^0) \times 100$$

wherein :

-  $i_{\text{corr}}^0$  = corrosion current without inhibitor

- $i_{\text{corr}}$  = corrosion current in the presence of a dose of inhibitor

The protection percentages (%P) obtained with the different compounds at concentrations varying from 1 to 200 ppm are given in Table 2. The study of the results shows that compounds A, E and I are the more efficient.

Table 2

Compound	Concentration of compound (ppm)	% P							
		1	2	5	10	20	50	100	200
A		69	92	97	98	97	98	98	98
B		14	36	76	95	97	98	98	98
C		04	10	07	29	66	86	90	89
D		00	16	19	36	57	59	68	77
E		39	66	95	95	96	97	97	99
F		23	23	64	83	91	97	97	98
G		28	13	31	53	81	86	96	96
H		06	46	65	56	73	94	99	98
I		26	33	93	96	97	97	97	97
J		21	40	61	83	96	96	96	97
K		03	03	00	16	32	45	57	63
L		00	00	05	15	35	55	70	80
M		00	26	68	81	92	94	96	97
N		36	58	78	83	89	95	97	97
O		53	63	81	85	89	93	96	96
P		05	45	67	80	90	94	96	97
Q		47	63	78	83	88	93	94	94
R		47	66	76	81	89	91	93	95
S		00	07	10	24	35	57	71	81
T		00	19	13	19	33	56	75	92

EXAMPLE 2

The procedure of Example 1 was followed by substituting  $\text{H}_2\text{S}$  for  $\text{CO}_2$ .

The protection percentages (%P) obtained with the different compounds at concentrations varying from 1 to 200 ppm are given in Table 2. The study of the results shows that compounds A, H and I are the more efficient.

5

Table 3

Compound	Concentration of compound (ppm)	% P							
		1	2	5	10	20	50	100	200
10	A	91	97	97	97	97	97	97	96
	B	63	75	89	90	91	93	95	96
	C	14	17	56	70	81	85	91	96
	D	07	08	23	30	53	88	96	98
	E	32	82	88	88	88	92	92	95
15	F	47	58	76	90	93	93	90	97
	G	42	41	71	88	90	86		
	H	20	90	96	96	98	98	98	98
	I	77	82	90	91	91	93	95	96
	J	69	82	85	90	94	94	97	99
20	K	54	72	85	85	85	83	89	89
	L	38	38	70	85	84	93	94	97
	M	54	64	65	71	84	92	97	97
	N	54	58	68	80	80	96	98	99
	O	44	45	55	66	81	93	98	98
25	P	51	52	71	80	89	91	96	98
	Q	00	14	28	37	57	82	90	94
	R	14	20	48	74	80	81	96	96

EXAMPLE 3 :

The corrosion inhibitory efficiencies in steel corrosion of compounds A and I under acidic conditions were estimated as following.

100 mg of compounds A and I, and lauryl amine (structure :  $C_{12}H_{25}NH_2$  ; produced by Wako Pure Chemical Industries, Inc.) and NYMEEN L202 (structure :

$C_{12}H_{25}N(C_2H_4OH)_2$  ; produced by NOF corporation) as controls were respectively added in a beaker containing 100 g of aqueous 5N HCl solution. Then, the beaker was placed in an ultrasonic cleaner (produced by Shibata Kagaku Kikai Kogyo Kabushiki Kaisha under trademark of "Model SU-3TH") and subjected to ultrasonication at 20°C for 5 minutes, to obtain a sample solution having the sample dispersed uniformly in the aqueous HCl solution. The pH of these sample solutions were not more than 1.

A steel plate (JIS G 3141 (SPCC-SB) ; cold-rolled steel plate of 1.0x30x50mm in size) was immersed in acetone, subjected to the similar ultrasonication as above, and washed with acetone by pouring. Then, the surface of the steel plate was thoroughly wiped with KimTowel<sup>R</sup>. The weight of the steel plate at this time was measured as a "weight of steel plate before (g)". Subsequently, the steel plate was immersed in the sample solution as prepared above and stood at room temperature for 5 hours. After this standing, the steel plate was extracted from the sample solution, immersed in ion-exchanged water, and subjected to the similar ultrasonication as above. Further, the steel plate was washed by pouring with ion-exchanged water and acetone in this order. The weight of the steel plate at this time was measured as a "weight of steel plate after (g)". The decreasing weight (g) was calculated from subtracting the weight of steel plate after (g) from the weight of steel plate before (g). From this decreasing weight, the corrosion-inhibiting percentage was calculated by the below formula. In this Example, the decreasing weight (g), when the use of sample was omitted, was 0.4652 g.

Corrosion-inhibiting percentage

$$= [(0.4652 \text{ g} - \text{decreasing weight (g) of each sample}) / 0.4652 \text{ g}] \times 100$$

The results are shown in Table 4.

Table 4

Sample	Amount added	Aqueous 5N HCl solution (g)	Weight of steel plate before (g)	Weight of steel plate after (g)	Decreasing weight	Corrosion-inhibiting percentage
None	0	100.06	11.4578	10.9926	0.4652	0
Lauryl amine	0.1119	99.98	11.3655	11.3363	0.0292	93.7
NYMEEN L202	0.1087	100.05	11.3624	11.2895	0.0729	84.3
Compound A	0.1009	101.52	11.364	11.358	0.0051	98.9
Compound I	0.1014	101.6	11.422	11.416	0.0057	98.8

It is note from the results of Table 4 that the compounds A and I according to this invention can exhibit excellent corrosion inhibitory efficiencies in steel corrosion as of near 99% even under such acidic conditions as of PH of not more than 1, compared with lauryl amine and NYMEEN L202 as controls showing the corrosion-inhibiting percentages under the same conditions of 93.7% and 84.3%, respectively.

10 EXAMPLE 4 : Preparation of composition for the protection of carbon steels

A composition formulated as follows was prepared :

	Parts by weight
Compound I .....	20
15 N-cocoaminepropionic acid (Surfactant) .....	20
Polyoxyethylenated cocoamine (11 EO units) (co-surfactant) .....	20
Butyl glycol .....	40

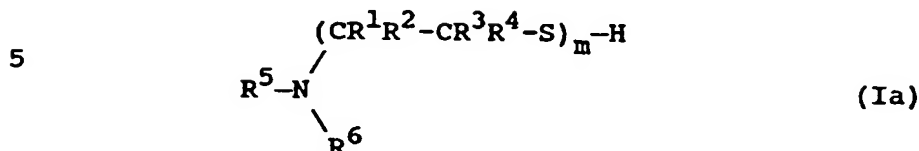
20 This composition, which is oil-soluble and aqueous-dispersible, can be continuously injected in corrosive fluids, using a dosing pump, at the rate of 10 to 20 ppm of the formulation with respect to the total volume of the fluid.

25 It can also be used to form a protective film at the rate of 100 to 1000 ppm during 2 hours. This film can be then maintained with a very low dose (of the order of 5 ppm).

30 For a "squeeze" treatment, the dose of composition to be injected may be in the range of 2 to 20% with respect to the fluid injected in the well as a plug.

CLAIMS

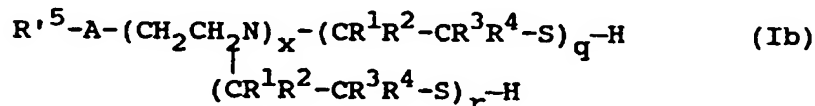
1 - Use of a mono- or polythiol selected among those of formula (Ia) :



wherein :

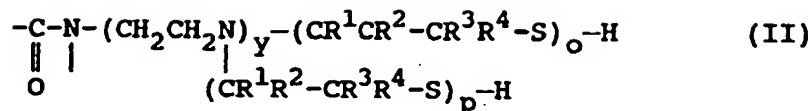
- 10 - each of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  independently stands for a hydrogen atom, an alkyl group having 1 to 10 carbon atoms or an aromatic group, it being possible for substituents  $\text{R}^1$  and  $\text{R}^3$  (or  $\text{R}^2$  and  $\text{R}^4$ ) to be mutually bound to form a hydrocarbon ring together with both carbon atoms which bear them ;
- 15 -  $\text{R}^5$  stands for a straight or branched alkyl or alkenyl group having 8 to 30 carbon atoms ; and
- $\text{R}^6$  stands for a straight or branched alkyl group having 1 to 30 carbon atoms, or a straight or branched alkenyl group having 2 to 30 carbon atoms, or a
- 20  $\text{-(CR}^1\text{R}^2\text{-CR}^3\text{R}^4\text{-S)}_n\text{-H}$  group ;
- $m$  and  $n$ , which are identical or different, each represent an integer in the range of 1 to 10, wherein the total number  $m + n$  of  $\text{-CR}^1\text{R}^2\text{-CR}^3\text{R}^4\text{-S-}$  chains,
- 25 identical or different, can be as high as 20 ;

and those of formula (Ib) :

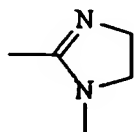


30 wherein :

- $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are as defined above ;
- $\text{R}'^5$  stands for a straight or branched alkyl or alkenyl group having 7 to 29 carbon atoms ; and
- A stands for a group (II) :



bound to R'<sup>5</sup> by -CO- ;  
or a group (III) :

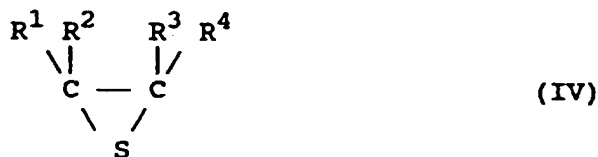


(III)

bound to R'<sup>5</sup> by the carbon atom ;

- x and y, identical or different, represent each 0 or an integer in the range of 1 to 10, with the proviso that  $1 \leq x + y \leq 10$  ;
- each of q, r, o and p is an average number of -CR<sup>1</sup>R<sup>2</sup>-CR<sup>3</sup>R<sup>4</sup>-S- chains, it being possible for said average number to be 0 and for said chains to be the same or different, for the "r" to be different if x is higher than 1 and for the "p" to be different if y is higher than 1, and "q +  $\sum$  r + o +  $\sum$  p" in the case where A is a group (II) or "q +  $\sum$  r" in the case where A is a group (III) is higher than 0 and can be as high as 30 ;

or of the adduct of at least one compound of formula (IV) :



wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are as defined above, to at least one compound having at least one group -NH<sub>2</sub> or

\ NH, selected among :

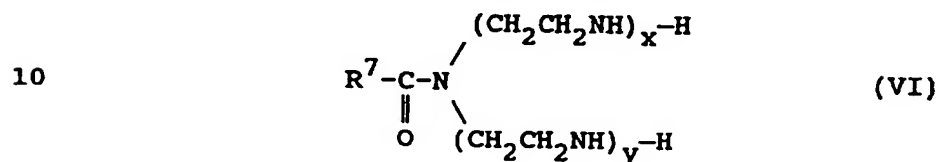
(a) aliphatic amines of formula (V) :



wherein :

- $R^5$  is as defined above ; and
- $R''^6$  stands for a hydrogen atom or a straight or branched alkyl group having 1 to 30 carbon atoms or a straight or branched alkenyl group having 2 to 30 carbon atoms ;

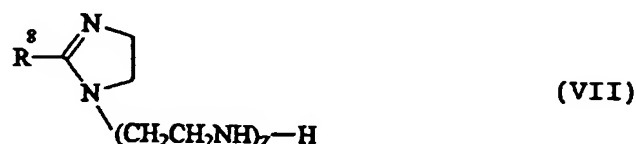
(b) amidoamines of formula (VI) :



wherein :

- $R^7$  has the same meaning as  $R'^5$  ;
- x and y are as defined above ; and

(c) imidazolines of formula (VII) :



wherein :

- $R^8$  has the same meaning as  $R'^5$  ; and
- z stands for 0 or is an integer in the range of 1 to 10 ;

as inhibitor of the corrosion of metals.

2 - Use according to Claim 1, wherein said inhibitor of the corrosion of metals used under acidic conditions of not more than pH 6.

3 - Use according to anyone of Claims 1 and 2 as inhibitor of the carbonic and/or sulfhydrylic corrosion of the carbon steels in the oil industries.

4 - Use according to anyone of Claims 1 to 3, characterized by the fact that, in the formula (Ia), the total number m + n is not in excess of 10.

5 - Use according to anyone of Claims 1 to 4, characterized by the fact that, in the formula (Ib),

" $q + \sum r + o + \sum p$ " in the case where A is a group (II) or " $q + \sum r$ " in the case where A is a group (III) is in the range of 0.5 to 10.

6 - Use according to anyone of Claims 1 to 5,  
5 characterized by the fact that each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  independently stands for a hydrogen atom, an alkyl group having 1 to 8 carbon atoms or a phenyl group, it being possible for  $R^1$  and  $R^3$  (or  $R^2$  and  $R^4$ ) to be mutually bound to form an alkylene chain.

10 7 - Use according according to anyone of Claims 1 to 4 and 6, characterized by the fact that, in the formula (Ia),  $R^5$  stands for the residue of a primary complex fatty amine, such as a copra chain or an oleic chain,  $R^6$  standing then for a  $-(CR^1R^2-CR^3R^4-S)_n-H$  group, the resulting dithiol  
15 being then under the form of a mixture ;  $R^5$  and  $R^6$  can also simultaneously stand for residues of a secondary complex fatty amine, the resulting monothiol being then under the form of a mixture.

8 - Use according to anyone of Claims 1 to 6,  
20 characterized by the fact that, in the formula (Ib),  $R'^5$  can also stand for the residue of an amide of a complex fatty acid, the resulting mono- or polythiol being then under the form of a mixture.

9 - Use according to anyone of Claims 1 to 3,  
25 characterized by the fact that the adduct is the adduct of at least one compound of formula (IV) to a mixture of compound (VI) and of compound (VII) consisting of a product of the dehydration condensation reaction of a fatty acid with a polyamine under production of an amidoamine and  
30 partial ring closure of the latter into imidazoline.

10 - Use according to anyone of Claims 1 to 3, characterized by the fact that the compound of formula (IV) is selected among ethylene sulfide, propylene sulfide, 1,2-dimethyl thiirane, 2,2-dimethyl thiirane, n-octyl  
35 thiirane, cyclohexene sulfide, styrene sulfide and 1,2-diphenyl thiirane.

11 - Use according to anyone of Claims 1 to 3, characterized by the fact that the amines of formula (V) are selected among decyl amine, undecyl amine, lauryl amine, myristyl amine, cetyl amine, stearyl amine, primary amines  
 5 derived from a fatty acid obtained from a coconut oil, primary amines derived from oleic acid, primary amines derived from a fatty acid obtained from a soybean oil, didecyl amine, diundecyl amine, dilauryl amine, dimyristyl amine, dicetyl amine, distearyl amine, secondary amines  
 10 derived from a fatty acid obtained from a coconut oil, secondary amines derived from oleic acid and secondary amines derived from a fatty acid obtained from a soybean oil.

12 - Use according to anyone of Claims 1 to 3, characterized by the fact that the amidoamines of formula (VI) are selected among :

- monoamide of lauric acid with ethylene diamine ;
  - amide of lauric acid with diethylene triamine ;
  - amide of lauric acid with triethylene tetramine ;
  - 20 - amide of lauric acid with tetraethylene pentamine ;
- and the analogous of amides with stearic acid, oleic acid, fatty acid derived from coconut oil and fatty acid derived from soybean oil.

13 - Use according to anyone of Claims 1 to 3, characterized by the fact that the imidazoline(s) of formula (VII) are selected among :

- . 2-undecyl imidazoline ;
- . 1-(2-aminoethyl)-2-undecyl imidazoline ;
- . 1-[N-(2-aminoethyl)-2-aminoethyl]-2-undecyl  
 30 imidazoline ;
- . 2-heptadecyl imidazoline ;
- . 1-(2-aminoethyl)-2-heptadecyl imidazoline ;
- . 1-[N-(2-aminoethyl)-2-aminoethyl]-2-heptadecyl  
 imidazoline ;
- 35 . imidazolines produced dehydration and ringclosure  
 of :

- . amide of lauric acid with tetraethylene pentamine ;
- . amide of stearic acid with tetraethylene pentamine ;
- 5 . monoamide of oleic acid with ethylene diamine ;
- . amide of oleic acid with diethylene triamine ;
- . amide of oleic acid with triethylene tetramine ;
- . amide of oleic acid with tetraethylene pentamine ;
- 10 . amide of fatty acid derived from coconut oil with triethylene tetramine ;
- . amide of fatty acid derived from coconut oil with tetraethylene pentamine ;
- . monoamide of fatty acid derived from soybean oil with ethylene diamine ;
- 15 . amide of fatty acid derived from soybean oil with diethylene triamine ;
- . amide of fatty acid derived from soybean oil with triethylene tetramine ;
- 20 . amide of fatty acid with tetraethylene pentamine.

14 - Use according to anyone of Claims 1 to 3, characterized by the fact that, in the adduct, the compound of formula (IV) has been added at the rate of 1 to 20 moles for 1 mole of (a) ; and from 0.5 to 30 moles for 1 mole of (b) or (c).

15 - Use according to anyone of Claims 1 to 3, characterized by the fact that the adduct is the adduct of 2 moles of ethylene sulfide to one mole of lauryl amine.

16 - Use according to anyone of Claims 1 to 3, characterized by the fact that the adduct is the adduct of about 2 to 3 moles of ethylene sulfide to 2-aminoethyl dodecanamide.

17 - Composition for the protection of metals against corrosion, particularly of carbon steels against carbonic and/or sulfhydric corrosion in oil industries, characterized by the fact that it consists or comprises a solution in at least one organic solvent of at least one

mono- or polythiol and/or at least one adduct such as defined in one of Claim 1 to 16, when it is intended to be used in a corrosive medium consisting of an oily phase, said composition further comprising at least one surfactant when  
 5 it is intended to be used in a corrosive medium consisting of an aqueous phase or consisting of an aqueous phase and an oily phase.

18 - Composition according to claim 17, intended to be used in a corrosive medium consisting of an oily phase  
 10 characterized by the fact that it consists of or by the fact it comprises for 100 parts by weight :

- (A) 20 to 50 parts by weight of at least one mono- or polythiol and/or at least one adduct such as defined in one of Claims 1 to 16 ; and
- 15 (B) 50 to 80 parts by weight of at least one organic solvent selected particularly among the alcohols such as those previously cited, the glycol mono- or di-ethers such as the di- or tri-ethylene glycol and the propylene glycol, petroleum fractions such as the white  
 20 spirit, the fuel oils, the kerosene and the naphtha.

19 - Composition according to Claim 17, intended to be used in a corrosive medium consisting of an aqueous phase or consisting of an aqueous phase and an oily phase, characterized by the fact it consists of or it comprises for  
 25 100 parts by weight of (A) + (B) + (C) :

- (A) 20 to 40 parts by weight of at least one mono- or polythiol and/or at least one adduct such as defined in anyone of Claims 1 to 16 ;
- 30 (B) 40 to 20 parts by weight of at least one organic solvent selected particularly among the glycol ethers, in particular the butyl glycol ; and
- (C) 20 to 40 parts by weight of at least one surfactant, selected particularly among aminoacides having a fatty chain and oxyethylenated derivatives of fatty amines.

35 20 - Method for the protection of metals against corrosion, particularly of carbon steels against carbonic and/or sulfhydrylic corrosion in oil industries, characterized

by the fact said metals are treated by a composition such as defined in anyone of Claims 17 to 19, at a temperature comprised between room temperature and 180°C, preferably of about 120°C.

5           21 - Method according to Claim 20, characterized by the fact the composition is continuously injected in corrosive fluids, using a dosing pump at the rate of 10 to 20 ppm of the formulation with respect to the total volume of the fluid.

10           22 - Method according to Claim 20, characterized by the fact the composition is used to form a protective film at the rate of 100 to 1000 ppm during 2 hours, it being possible for this film to be maintained with a very low dose of the order of 5 ppm.

15           23 - Method according to Claim 20, characterized by the fact that a "squeeze" treatment is conducted according which the dose of composition to be injected may be in the range of 2 to 20% with respect to the fluid injected in the well as a plug.



Application No: GB 9807791.0  
Claims searched: 1-23

Examiner: Gavin Dale  
Date of search: 27 July 1998

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C1C (CACE)

Int Cl (Ed.6): C23F 11/16

Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0243016A1 (EXXON CHEMICAL PATENTS INC) See page 2 - summary of invention	17
X	EP 0046139A1 (CIBA-GEIGY AG) See page 2 lines 1-15	17

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.